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① **CANADIAN PATENT**

㉔ PROCESS FOR FLUORINATING HALOHYDROCARBONS

Frederic W. Swamer, Boothwyn, Pennsylvania, U.S.A.,
and Benjamin W. Howk, West Chester, Pennsylvania,
U.S.A.

Granted to E.I. du Pont de Nemours and Company,
Wilmington, Delaware, U.S.A.

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This invention relates to a process for catalytic vapor phase fluorination of halohydrocarbons and more particularly to the substitution of fluorine for other halogens in halohydrocarbons which contain halogens other

5 than or in addition to fluorine, employing an improved catalyst for such reaction.

The process of this invention is applicable to the preparation of a large number of fluorinated compounds which in general are well known and are valuable for a wide

10 variety of purposes such as refrigerants, propellents, dielectrics, general inert solvents, selective solvents in extraction operations, and compounds characterized by stability to high temperatures and chemical attack. Many of the lower boiling products such as dichlorodifluoro-

15 methane, chlorotrifluoromethane and trichlorofluoromethane are well known and have been widely used as refrigerants and as propellents. More highly fluorinated or completely fluorinated compounds of the aliphatic series, such as carbon tetrafluoride, chloropentafluoroethane, hexafluoro-

20 ethane, chloroheptafluoropropane, octafluoropropane, perfluorobutane, and perfluorocyclobutane are known and are recognized as being useful as refrigerants and propellents but they have not been readily available, particularly at low cost, because they have been difficult

25 to make and have been obtainable only by complex and expensive procedures. One procedure for producing carbon

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tetrafluoride, for example, comprises two steps: the con-
version of dichlorodifluoromethane to chlorotrifluoromethane
over alumina and then the fluorination of chlorotrifluoro-
methane over chromium fluoride to produce carbon tetra-
5   fluoride.

The catalysts commonly used for replacing chlorine
and bromine by fluorine in making fluoromethanes and fluoro-
ethanes, have included antimony pentahalides, chromium oxy-
fluorides, chromium fluoride, aluminum fluorides, activated
10   carbon, and aluminum oxide impregnated with metal halides.
While commercial processes have been developed for employing
such catalysts, such processes have been quite limited in
efficiency, in economy of operation, and in the extent to
which the fluorination of the halohydrocarbon could be
15   induced to proceed. Usually complete fluorination is
obtained with considerable difficulty and to only a limited
extent, resulting in low yields of the desired product
and high costs.

It is an object of this invention to provide a
20   process for fluorinating halohydrocarbons of the aliphatic
series which contain 1 or more halogen atoms other than
or in addition to fluorine so as to partially or completely
replace such other halogen atoms by fluorine. Another
object is to provide a catalytic vapor phase process for
25   reacting anhydrous hydrogen fluoride with halogenated
aliphatic hydrocarbons so as to replace halogen atoms
therein other than fluorine in the presence of an improved
and highly active and efficient catalyst. A further object

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is to provide such a process which is practical, efficient, economical and simple and easy to operate and control, su as to obtain high yields of the desired products. Still other objects will appear hereinafter.

5   The above and other objects may be accomplished by the process of this invention which comprises contacting a vapor mixture of a halogenated aliphatic hydrocarbon of 1 to 8 carbon atoms in which adjacent carbons are linked solely by 1 to 2 valence bonds and in which the halogen

10   atoms have an atomic weight of less than 80 and include at least one halogen atom having an atomic weight between 35 and 80 and at least a stoichiometric proportion of anhydrous hydrogen fluoride with a catalyst which consists essentially of an activated anhydrous chromium (III) oxide

15   at a temperature in the range of from about 150°C. to about 700°C. such that the principal reaction is the substitution of fluorine for other halogen of the halogenated hydrocarbon, and separating the fluorinated compound from the reaction mixture.

20   It has been found that the catalysts of the character above specified are exceptionally active and efficient in such process to cause the hydrogen fluoride to react with the halogenated hydrocarbons of the specified class so that fluorine is substituted for chlorine and bromine

25   to produce the desired fluorinated or more highly fluorinated products in unusually high yields and without requiring excessively high temperatures. The process is readily controlled to produce any desired degree of fluorine substitution and is particularly effective for the complete

replacement of other halogens by fluorine, especially for the preparation of fluorocarbons from other completely halogenated hydrocarbons.

The process is simple and easily carried out by passing a gaseous mixture of anhydrous hydrogen fluoride and the halogenated hydrocarbon over or through the catalyst maintained at the desired temperature in a conventional reactor of the type commonly employed for reactions of this character. Usually, the gaseous mixture will be passed through a bed of the catalyst in a reaction tube. The reaction tube may be constructed of any metal or other material that is inert to anhydrous hydrogen fluoride, hydrogen chloride and hydrogen bromide at temperatures up to 700°C. and is resistant to heat for extended periods of time. Suitable materials for construction of the reaction tube include nickel alloys sold under the trade marks "Hastelloy" C and "Inconel" which are hereinafter identified by said trade marks, nickel, stainless steel, platinum, and fused refractory alumina such as alundum.

The halogenated aliphatic hydrocarbons which may be fluorinated by the process of this invention are those which contain 1 to 8 carbon atoms and in which adjacent carbon atoms are linked solely by 1 to 2 valence bonds. These include the saturated compounds, such as halogenated alkanes and halogenated cycloalkanes, and unsaturated compounds, such as the halogenated alkenes and halogenated cycloalkenes. Preferably, the halogenated hydrocarbons are the acyclic compounds, such as the halogenated alkanes and halogenated alkenes, and particularly the saturated acyclic halogenated hydrocarbons. The halogen atoms in the

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halogenated hydrocarbons are those which have an atomic
weight of less than 80, i.e. fluorine, chlorine and bromine,
and include at least one halogen atom having an atomic
weight between 35 and 80, i.e. chlorine and bromine. The
5 halogenated hydrocarbons may be partially or completely
halogenated, that is, from one to all of the hydrogen atoms
will be replaced by halogen atoms, including at least one
of chlorine and bromine. The compounds that may be fluori-
nated by the process of this invention include the following
10 which for convenience are presented in groups having members
that are related in composition or in structure.

Group I - Chloro- and bromoalkanes of the general formula

$C_mH_nX_y$ where $m = 1-8$, $n + y = 2m + 2$, and

$X = Cl$ or Br.

15 Representatives:

CH_3Cl	CH_3Br	
CH_3CH_2Cl	CH_3CH_2Br	
$CH_3CH_2CH_2CH_2Cl$	$CH_3CH_2CH_2CH_2Br$	
CH_2Cl_2	CH_2Br_2	CH_2ClBr
CH_3CHCl_2	CH_3CHBr_2	$CH_3CHClBr$
$ClCH_2CH_2Cl$	$BrCH_2CH_2Br$	$BrCH_2CH_2Cl$
$CHCl_3$	$CHBr_3$	$CHClBr_2$
CH_3CCl_3	CH_3CBr_3	$CHCl_2Br$
$ClCH_2CHCl_2$		
CCl_4		
CCl_3CCl_3		

Group II - Chloro-, bromo-, fluoroalkanes of the general

formula $C_mH_nBr_xCl_yF_z$ where m = 1-8, n + x + y + z =
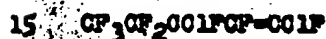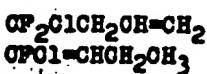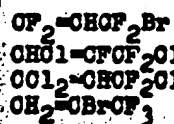
2m + 2, x + y is at least one, and z is at least one.

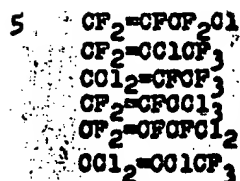Representatives:

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CF_3Cl	CF_2Cl_2	$CFCl_3$
CF_3Br	CF_2Br_2	$CFBr_3$
	CF_2BrCl	$CFBrCl_2$
		$CFBr_2Cl$
$CHFBrCl$	CHF_2Cl	CHF_2Br
$ClCF_2CF_2Cl$	$BrCF_2CF_2Br$	$ClCF_2CF_2Br$
CF_3CFCl_2	CF_3CFBr_2	$CF_3CFBrCl$

10 Cl_2CFCF_2Cl

$BrCF_2CF_2CF_2CF_2Br$	$ClCF_2CF_2CF_2CF_2Cl$
$BrCF_2CF_2CF_2CF_2Cl$	$Br(CF_2)_6Br$
$CF_3CFBrCF_2CF_3$	$CF_3CFClCF_2CF_3$
$CF_3CFBrCFClCF_3$	$CF_3CClFCClFCF_3$

15

$CF_3(CF_2)_7Br$	$Br(CF_2)_8Br$	$Cl(CF_2)_8Cl$
$Cl_3C(CF_2)_2Cl$	$Cl_3C(CF_2)_6Cl$	$Cl(CF_2)_6H$
$ClCF_2CFClCF_3$	$BrCF_2CFBrCF_3$	

Group III - Chloro-, bromo-, and fluoroalkenes containing

at least one halogen other than fluorine.

20 Representatives:

$CF_2=CFBr$	$CF_2=CFCl$
$BrCF=CFBr$	$ClCF=CFCl$
$CF_2=CBr_2$	$CF_2=CCl_2$
$CFBr=CBr_2$	$CFCl=CCl_2$

25

$CFBr=CHF$	$CFCl=CBr_2$
$CF_2=CHBr$	$CHCl=CF_2$
$CFBr=CHBr$	$CHF=CHCl$

$Cl_2C=CCl_2$ $CH_2=CCl_2$
$ClCH=CCl_2$ $CH_2=CBr_2$
$ClCH=CHCl$
$CH_2=CHCl$

5   $CF_2=CFCF_2Cl$ $CF_2ClCF=CFCF_2Cl$
    $CF_2=CClCF_3$
    $CCl_2=CFCF_3$ $CF_2=CFCFClCF_2Cl$
    $CF_2=CFCCl_3$
    $CF_2=CFCFCl_2$
    $CCl_2=CClCF_3$

    $CF_2=CHCF_2Br$ $CF_2ClCH_2CH=CH_2$
    $CHCl=CFCF_2Cl$ $CFCl=CHCH_2CH_3$
    $CCl_2=CHCF_2Cl$
    $CH_2=CBrCF_3$

15   $CF_3CF_2CClFCF=CClF$

Group IV - Cyclicalkanes and cyclicalkenes containing at least one halogen other than fluorine.

$\overline{CCl_2-CCl_2-CF_2-CF_2-CF_2}$

$\overline{CF_2(CF_2)_4CFBr}$

20   $\overline{CFCl(CF_2)_4CF_2}$

$\overline{CFCl-CFCl-(CF_2)_3-CF_2}$ $\overline{CF_2CCl_2-CFCl-CCl=CCl}$

                              $\overline{CF_2-CFCl-CF_2CCl=CCl}$

$\overline{CF_2CFBrCFBrCF_2CF=CF}$

$\overline{CF_2CCl_2CCl_2CCl=CCl}$

25   $\overline{CF_2CCl_2CFClCCl=CCl}$
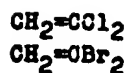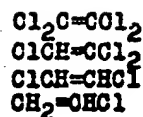
The process of this invention is also applicable to the fluorination of phenyl, halophenyl and halomethyl-phenyl substituted halomethanes such as
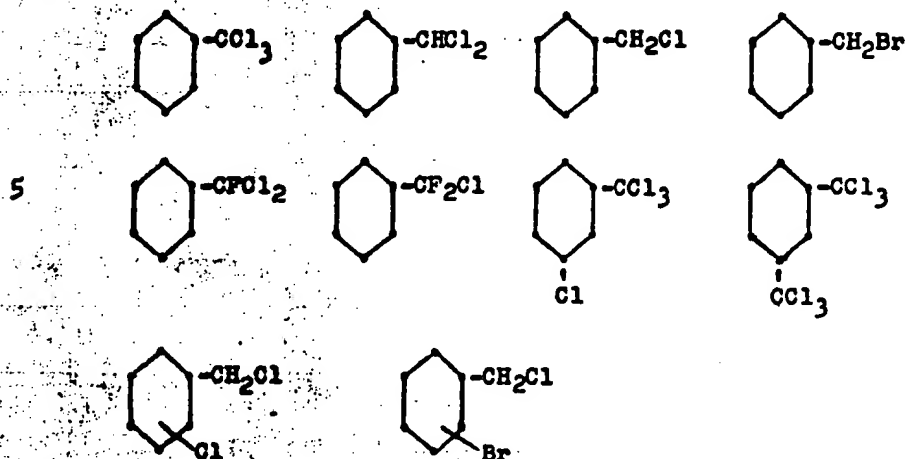
In the fluorination of these compounds, the halogens, other than fluorine, in the halomethyl groups are replaced by fluorine but the halogen substituents on the benzene ring remain intact.

By the process of this invention the chlorine and/or bromine of the halogenated hydrocarbons are partially or completely replaced by fluorine due to reaction with hydrogen fluoride to provide halogenated hydrocarbons which contain a higher proportion of fluorine than the starting material. In some cases, compounds, other than the products of direct replacement, are obtained in minor proportions as the result of secondary disproportionation reactions occurring in the process.

The catalysts employed in this process consist essentially of an activated anhydrous chromium (III) oxide. In other words, except for diluents, carriers, and minor proportions of impurities, they consist of Cr_2O_3 and have

5   been activated by heating in an inert atmosphere at a temperature of from about 400°C. to about 600°C., preferably about 500°C. Inert atmospheres include nitrogen, air, steam, and anhydrous hydrogen fluoride, nitrogen being preferred. The catalysts are practically inert toward

10   gaseous anhydrous hydrogen fluoride, oxidation by air, and reduction by hydrogen at the temperatures employed in this process. Treatment of the catalysts with gaseous anhydrous hydrogen fluoride for extended periods of time at such temperatures has not significantly affected their

15   activity as catalysts and does not convert the Cr_2O_3 to an oxyfluoride, i.e. a basic chromium fluoride. For example, a representative activated chromium (III) oxide gel catalyst of this invention, after being used for 180 hours in the process of this invention, contained only 2.3% by weight

20   of fluorine and was not converted to an oxyfluoride. This stability of the catalysts of this invention imparts to the catalyst a long, useful life which maintains the efficiency and lowers the cost of the fluorination process. While the catalysts of this invention consist essentially

25   of activated anhydrous chromium (III) oxide (activated Cr_2O_3), they vary somewhat in activity with the source and the method of preparing the chromium (III) oxide.

The preferred catalyst for the process of this invention is the so-called gel-type activated chromium (III) oxide obtained by reducing chromium trioxide (CrO_3) and dehydrating the reduced product in the manner disclosed by Ruthruff in "Inorganic Syntheses", Vol. II, pp. 190-193, published in 1946 by McGraw-Hill Book Co., New York, and by Turkevich and Ruthruff in U.S. Patent 2,271,356. More particularly the preferred catalyst is prepared by dissolving chromium trioxide in water, gradually adding ethanol or

10 other suitable reducing agent to the solution and heating under reflux conditions until the chromium oxide gel precipitates, separating the gel from the reaction mixture, drying it, and then dehydrating and activating the product by heating it at a temperature of from about 400° C. to about 600° C. in an inert atmosphere until the water is removed and an anhydrous product is obtained. The preferred process for preparing this "gel-type" catalyst is described in detail in part A of Example 1 given hereinafter. Analyses of several batches of catalysts so made and dehydrated at

20 500° C. under nitrogen have ranged between 67% and 68% chromium. One batch analyzed 68.3%, 68.4% chromium. The calculated amount of chromium in Cr_2O_3 is 68.5%.

The gel-type catalyst so produced is characterized by an exceptionally high activity whereby, for example, dichlorodifluoromethane and carbon tetrachloride, respectively, are converted to carbon tetrafluoride in a single step by reaction with hydrogen fluoride at from about 300° C. to about 600° C. and carbon tetrachloride is similarly converted to dichlorodifluoromethane at from about 150° C.

to about 250°C. The activated anhydrous chromium (III)
oxide gel catalyst as so prepared is generally of a particle
size suitable for use as the fluorination catalyst in a
tubular reactor. However, if desired, it may be passed
5   through a screen or series of screens to obtain material
having a particular range of particle size. The particularly
convenient size is 10 mesh to 20 mesh, although particle
sizes smaller and larger than this may be used. Also the
dry catalyst may be pulverized and the resulting powder
10 mixed with a suitable binding agent such as powdered poly-
tetrafluoroethylene and pressed into pellets which may be
used to form the catalyst bed for use in the process of
this invention.

Another effective activated chromium (III) oxide
15 catalyst of this invention, although somewhat less active
than the gel-type activated chromium (III) oxide prepared
from chromium trioxide, is the chromic oxide, Cr_2O_3,
obtained by dehydrating the commercial pigment known as
Guignet's Green, having the composition $Cr_2O_3 \cdot 2H_2O$ at from
20 about 400°C. to about 600°C. in an inert atmosphere. The
dehydration of Guignet's Green to prepare it for use as
an activated fluorination catalyst is described in detail
in Example 3 hereinafter. The Guignet's Green is preferably
dehydrated and activated under nitrogen. When it is
25 dehydrated at 500°C. with free access to air, it has less
catalytic activity than when it is dehydrated in nitrogen.
Whereas the nitrogen-dehydrated material gives high con-
versions of dichlorodifluoromethane to carbon tetrafluoride
at 500°C., the air-dehydrated product converts dichlorodi-
30 fluoromethane mainly to chlorotrifluoromethane at this

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temperature. The chromium oxide gel, made from chromium

trioxide, does not exhibit this effect of contact with air

during dehydration. Although the chromium oxide gel is

commonly dehydrated under nitrogen, it may be dehydrated

5   in air and retain its high catalytic activity so that di-

chlorodifluoromethane may still be converted to carbon

tetrafluoride in its presence.

Another source of an activated catalytic chromium

(III) oxide, for use in the fluorination of halogenated

10   aliphatic compounds by the process of this invention, is

water-soluble chromium (III) salts which are precipitated

with ammonium or alkali metal hydroxide to yield chromium

hydroxides that are washed and dehydrated to provide an

activated chromic oxide. In Example 9 hereinafter, a

15   description of a preferred mode of preparation of such an

activated chromium (III) oxide from chromium (III) chloride

hydrate and ammonium hydroxide and the effect of its use

in fluorinating dichlorodifluoromethane to chlorotrifluoro-

methane and carbon tetrafluoride are given. Besides chromium

20   (III) chloride, other water-soluble chromium (III) salts,

such as the acetate, nitrate, and sulfate, may be used.

Besides ammonium hydroxide, sodium or potassium hydroxide

may be used to precipitate the chromium in the form of its

hydroxide from a water solution of one of its salts. After

25   being washed to remove the extraneous ionic material and

being dehydrated, the resulting activated chromium (III)

oxide may be used as a fluorination catalyst in the process

of this invention.

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        The various foregoing forms of activated chromium

(III) oxide may be passed through sieves of suitable sizes

to obtain a range of desired particle sizes, and the

powdered material may be pressed into pellets with a binder

5   such as polytetrafluoroethylene.

        The activated chromium (III) oxide catalyst may

be supported on an inert substrate, such as alumina,

including the so-called "activated alumina". For example,

alumina, in the form of spheres about 1/4" to 1/16" in

10 diameter or of irregular granules of about 8 to 15 mesh

in size, may be mixed with a water solution of a chromium

compound and the chromium oxide precipitated on the alumina,

treating the alumina mixture essentially as the chromium

solution is treated above to provide activated chromium (III)

15 oxide in the absence of the alumina. For example, the

alumina may be mixed with chromium trioxide and the trioxide

reduced to an insoluble chromium oxide with ethanol or the

alumina may be mixed with a solution of chromium (III)

nitrate and chromium hydroxide precipitated with the

20 ammonium hydroxide and the chromium hydroxide washed with

water. The mixture will then be dehydrated to form activated

chromium (III) oxide on the alumina. Catalysts, in the form

of activated chromium (III) oxide admixed with aluminum

oxide, are known to the art for use in the treatment of

25 petroleum, particularly for the catalytic conversion of

hydrocarbons and such catalysts may be used in the process

of this invention, although they are somewhat less active

and efficient than the catalyst prepared from the gels

obtained in the reduction of chromium trioxide and those

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prepared from Guignet's Green. Representative catalysts
of this type and the methods for preparing them are dis-
closed by Thomas in Patent 2,402,854. A suitable catalyst
of this type is the chrome-alumina catalyst made and dis-
tributed by The Harshaw Chemical Company for use in the
petroleum industry, the use of which catalyst is illustrated
in Example 10 given hereinafter.

For practical purposes, such as eliminating or
minimizing the corrosion of equipment, anhydrous hydrogen
fluoride is preferred. Small amounts of water, up to 0.1%,
in the hydrogen fluoride can be tolerated, since gaseous
hydrogen fluoride is fed to the reactor for the fluori-
nation at an elevated temperature, and small amounts of
water that might be carried into the reactor with the
hydrogen fluoride are not deleterious. Commercial anhydrous
hydrogen fluoride, which may contain traces of sulfur com-
pounds, appears quite as satisfactory for the reaction as
pure material.

The molar ratio of anhydrous hydrogen fluoride to
the halogenated aliphatic hydrocarbon to be fluorinated
may be varied over the range of 1 mole to 10 moles of
hydrogen fluoride for each mole of the halogen compound,
the preferred ratio being determined by the nature of the
halogen compound to be fluorinated and by the amount of
fluorination desired. In fluorinating carbon tetrachloride
to carbon tetrafluoride, for example, 4 moles of hydrogen
fluoride per mole of carbon tetrachloride are required.

In converting vinyl chloride to vinyl fluoride, only one
mole of hydrogen fluoride per mole of vinyl chloride is
required. When the intent is to produce carbon tetrafluoride
from carbon tetrachloride, a lower molar ratio of reactants
5 than 4 moles of hydrogen fluoride per mole of carbon tetra-
chloride results in a decreased output of carbon tetra-
fluoride and an increase in conversion to only partially
fluorinated products such as chlorotrifluoromethane, di-
chlorodifluoromethane, and trichlorofluoromethane. Usually,
10 an amount of hydrogen fluoride is used that is at least
the stoichiometric amount needed for a given fluorination,
preferably about a 50% molar excess.

The feed rate, expressed as parts by weight of
halogenated aliphatic hydrocarbon (exclusive of hydrogen
15 fluoride) per part of catalyst per hour, may vary from
about 0.1 part to about 2.0 parts, with a feed rate of
about 0.5 part being preferred. Since the fluorination is
exothermic, the upper limit of the feed rate is determined
by the efficiency of the dissipation of the heat of reaction
20 from the reaction zone as well as by the reactivity and
molecular weight of the halogenated aliphatic reactant.
Too fast a feed rate may result in the generation of more
heat than is withdrawn. Such a condition causes the catalyst
temperature to rise, and the course of the reaction may
25 change. Too slow a feed rate fails to use the total capacity
of the catalyst and of the cooling system, resulting in low
operation efficiency, and it could result in such a prolonged
exposure of the organic material to the elevated temperature
that decomposition or undesirable alteration would occur.

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The broad temperature range in which the fluorination of chloro or bromo aliphatic hydrocarbons may be effected with hydrogen fluoride is from about 150°C. to about 700°C. Narrower temperature ranges within these

5 limits are found to be suitable for a selected degree of fluorination of a particular halogenated hydrocarbon and for a fluorination of a specific compound using a given type or form of activated chromium (III) oxide catalyst. For example, the essentially complete conversion of carbon

10 tetrachloride to dichlorodifluoromethane occurs at 150°C. with the gel-type activated chromium (III) oxide catalyst prepared from chromium trioxide, while a similar conversion using activated chromium (III) oxide prepared from Guignet's Green requires a temperature of about 250°C. In brief,

15 the temperature at which the process is run, other conditions being the same, depends upon the product that is desired from a given starting material that is to be fluorinated. Temperatures, below the preferred range for a particular product from a given material, result in low conversions

20 and hence decreased efficiency of operation, and temperatures, above the preferred range, give rise to an over-fluorination for the desired product when over-fluorination is possible with the particular halohydrocarbon employed.

The new fluorination process is usually run at

25 essentially atmospheric pressure or under the pressure induced by the hydraulic head of scrubbers and by beds of drying agents for a gas stream. The operation of the process need not be limited to these pressure conditions and the reaction may be run under super- or sub-atmospheric

30 pressures.

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In order to more clearly illustrate this invention, preferred modes of carrying the same into effect, and advantageous results obtained thereby, the following examples are given in which the proportions of materials

.5 employed and produced, are by volume except where specifically indicated otherwise.

Example 1

(A) Preparation of activated chromium (III) oxide gel catalyst.

A 12-liter round-bottom flask, equipped with an

10 agitator, reflux condenser, and dropping funnel, is charged with 6 liters of distilled water and 460 g. of chromium trioxide (CrO_3). The mixture is stirred to dissolve the chromium trioxide and, with rapid agitation, 240 ml. of 95% ethanol is added in 30 ml. increments, each at a 5-

15 minute interval. The solution is then allowed to stand for 3 hours, after which an additional 240 ml. of 95% ethanol is added in increments as before. The mixture is then heated to reflux and refluxed vigorously with agitation for 16 hours. During refluxing, chromium oxide gel pre-

20 cipitates. The mixture is cooled to room temperature and filtered in a 26 cm. Buchner funnel. Air is drawn through the filter cake until the cake becomes dry enough to crack. The filter cake is further dried in a vacuum oven for 48 hours to 60 hours at 40°C. to 50°C. and finally for 12 hours

25 to 24 hours at 80°C. to 90°C. The product so obtained is dark brown-black and weighs about 500 g. Although it appears to be dry, it may contain 30% to 40% of water.

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This residual water is removed and the chromium oxide
activated by heating the chromium oxide at 500°C. in a
nitrogen atmosphere for about 7 hours. The dehydrated
material is passed through sieves to obtain for use material
5   that is between 10-mesh and 20-mesh in size. This prepa-
ration, except for passage of the material through the
sieves and for changes in the drying and dehydrating pro-
cedure, is given in Inorganic Syntheses, Vol. II, pp. 190-
193 (1946).

10   (B) <u>Fluorination of carbon tetrachloride at 150°C.</u>

Activated chromium (III) oxide gel (76.8 g.),
prepared as described above, was placed in a 1" internal
diameter Hastelloy C reactor tube heated electrically and
connected with a potassium hydroxide scrubber and with a
15   drying tube containing successive beds of anhydrous soda
lime, calcium chloride, and calcium sulfate. The catalyst
was heated to 150°C., and a mixture of carbon tetrachloride
and anhydrous hydrogen fluoride passed through the catalyst
bed at the rate of 0.25 g. of carbon tetrachloride per gram
20   of catalyst per hour and with a ratio of 8 to 9 moles of
HF to each mole of CCl_4. The exit gases from the reactor
were scrubbed with 10% potassium hydroxide solution, dried,
and analyzed. The resulting gaseous product was found by
mass spectrometry to comprise by volume 97% dichlorodifluoro-
25   methane and 2.1% chlorotrifluoromethane.

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Example 2

Fluorination of carbon tetrachloride at 400°C.

The procedure described in Example 1 was repeated
except that the catalyst was heated to 400°C., the carbon
5   tetrachloride feed rate was 0.2 g. CCl_4/g. catalyst/hr., and
the HF/CCl_4 mole ratio was about 10/1. After scrubbing the
gaseous effluent from the reactor with 10% potassium hydrox-
ide followed by drying, the remaining gas was found by mass
spectrometry to consist of 94% carbon tetrafluoride and
10   3.2% chlorotrifluoromethane by volume.

When the CCl_4 feed rate was increased to 0.69 g.
CCl_4/g. catalyst/hr. and the HF/CCl_4 mole ratio kept at
about 8/1 while holding the catalyst temperature at 400°C.,
the scrubbed and dried gaseous product contained 94.5%
15   carbon tetrafluoride and 5.2% chlorotrifluoromethane.

Example 3

Fluorination of carbon tetrachloride - Catalyst from Guignet's Green

An activated chromium (III) oxide catalyst, Cr_2O_3,
was prepared by heating commercial Guignet's Green,
20   $(Cr_2O_3 \cdot 2H_2O)$ at 500°C. under a slow stream of nitrogen for
a period of 7 hours.

A one-inch internal diameter Hastelloy C reactor
was charged with 180 grams of 4 to 8 mesh activated chromium
(III) oxide prepared as described in the preceding paragraph.
25   Anhydrous hydrogen fluoride was passed through the catalyst
at a rate 21 to 25 g./hr. for about 30 minutes at 500°C.
and then cooled. Under an atmosphere of nitrogen, the
catalyst was heated to 200°C. While holding the temperature

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of the catalyst between 198°C. and 204°C., a mixture of carbon tetrachloride and anhydrous hydrogen fluoride was fed to the reactor to supply 0.12 g. of CCl_4 per gram of catalyst per hour and about 8 moles of HF per mole of CCl_4.

5 The gaseous effluent from the reactor was scrubbed with 10% potassium hydroxide solution and dried. A sample of the resulting gaseous product comprised 83.5% dichlorodifluoromethane, 15.3% trichlorofluoromethane, 0.6% chlorotrifluoromethane, and 0.6% nitrogen as determined by mass spectrometry.

10 When the CCl_4 feed to the reactor was increased to 0.31 g. CCl_4/g. catalyst/hr. and the HF/CCl_4 molar ratio was reduced to about 3/1, the scrubbed and dried gaseous product comprised 68.9% dichlorodifluoromethane, 30.6% trichlorofluoromethane, and 0.5% chlorotrifluoromethane.

15 ### Example 4

Fluorination of chloroform

A one-inch internal diameter Hastelloy C reactor was charged with about 77 grams of the activated chromium (III) oxide catalyst prepared as described in Example 1 (A).

20 The catalyst bed was heated to 400°C. in a nitrogen atmosphere. While maintaining the temperature at 400°C., a mixture of chloroform and anhydrous hydrogen fluoride was fed to the reactor to supply 0.5 g. $CHCl_3$/g. catalyst/hr. and about four moles of HF per mole of $CHCl_3$. The effluent

25 product, after scrubbing and drying, comprised 96.2% trifluoromethane, 0.5% dichlorofluoromethane, 0.5% chlorodifluoromethane, and 0.3% chloroform as determined by mass spectrometry.

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When the chloroform feed to the reactor was increased to 0.82 g. $CHCl_3$/g. catalyst/hr. while maintaining the $HF/CHCl_3$ mole ratio at about 4/1, the scrubbed and dried effluent gas still contained 96.2% trifluoromethane and small amounts of lesser fluorinated methanes.

Example 5

Fluorination of methyl chloride

An activated chromium (III) oxide catalyst (73 g.), prepared as described in Example 1 (A), was placed in a one-inch Hastelloy C reactor. The catalyst bed was maintained at a temperature of 250°C, while methyl chloride was fed to the reactor at a rate of 0.25 mole/hr. along with HF at a rate of 1.25 moles/hr. The effluent gas from the reactor was scrubbed with 10% KOH solution, dried, and analyzed by mass spectrometry. It was found to contain 6.5% of methyl fluoride and 89.7% of methyl chloride, along with small amounts of other organic compounds.

Example 6

Fluorination of dichlorodifluoromethane

A Hastelloy C reactor one inch in internal diameter was charged with 70 grams of the activated chromium (III) oxide catalyst prepared as described in Example 1 (A). A mixture of anhydrous hydrogen fluoride and dichlorodifluoro-methane in a mole ratio of 4 to 1 was passed at different feed rates over the catalyst bed at different temperatures. The exit gases from the reactor were scrubbed with 10% potassium hydroxide solution and dried over anhydrous soda-lime, calcium chloride, and calcium sulfate. The variation in the composition of the effluent gases as determined by gas chromatography is shown in the following table.

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Temp. of catalyst, °C.	Feed Rate, g. CCl$_2$F$_2$/g. catalyst/ hr.	Composition of Product, % by vol.		
		CF$_4$	CClF$_3$	CCl$_2$F$_2$
200	0.37	-	67-76	33-24
300	0.37	67-68	33-32	-
400	1.60	97	ca. 3	-
500	0.58	98	small amt.	-

These results show how the activity of the activated chromium
(III) oxide catalyst is affected by temperature and how the
degree to which the dichlorodifluoromethane becomes further
fluorinated is controlled mainly by the temperature. The
data show also that essentially quantitative replacement
of the chlorine by fluorine is attained at 400°C. with a
high feed rate or throughput of reactants.

At a temperature of 500°C., a mixture of anhydrous
hydrogen fluoride and dichlorodifluoromethane in a mole ratio
of about 4 to 1 was passed through the reactor with catalyst
as described above at the rate of 0.35 g. CCl$_2$F$_2$/g. catalyst/
hr. for a total period of 180 hours. Throughout the
operation under these conditions, the dichlorodifluoromethane
was 98% to 99% converted to carbon tetrafluoride.

In the absence of any catalyst, a mixture of an-
hydrous hydrogen fluoride and dichlorodifluoromethane in a
mole ratio of 4 to 1 was passed through a 1" x 30" Hastelloy
C reactor at 550°C. and at 600°C. at the rate of 0.25 gram
mole of CCl$_2$F$_2$ per hour. The effluent product was scrubbed
with 10% potassium hydroxide solution to remove hydrogen
fluoride, dried, and analyzed in a mass spectrometer.

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At 550°C., the dichlorodifluoromethane was 10% converted to chlorotrifluoromethane and, at 600°C., the conversion was 35%. No carbon tetrafluoride was detected in the products.

5

Example 7

Fluorination of dichlorodifluoromethane - Catalyst from Guignet's Green

A one-inch internal diameter Hastelloy C reactor which contained 184 grams of 4 to 8 mesh Guignet's Green was heated at 500°C. for two hours under a slow stream of nitrogen to dehydrate the chromium oxide. A mixture of anhydrous hydrogen fluoride vapor and nitrogen was then passed through the reactor for two more hours with the temperature held at 500°C. At this temperature and at succeeding lower temperatures, dichlorodifluoromethane, at a rate of 0.25 gram-mole per hour, mixed with anhydrous hydrogen fluoride, at a rate of 1 gram-mole per hour, was passed through the reactor. The effluent gas from the reactor was scrubbed with 10% potassium hydroxide solution, dried, and analysed by mass spectrometry. The results of the analyses are set forth in the following table.

Temp. of catalyst, °C.	Composition of Product, % by vol.	
	CF_4	$CClF_3$
500	92	8
400	48	52
300	-	99.7
200	-	Trace

The complete exchange of the chlorine in dichloro-
difluoromethane by fluorine is effected at about 500°C.,
while a partial replacement of the chlorine occurs at 300°C.
to provide the single product chlorotrifluoromethane. Thus,
merely by suitably changing the reaction temperature,
essentially quantitative yields of trifluorochloromethane
and tetrafluoromethane may be obtained as desired.

Example 8

Fluorination of dichlorodifluoromethane - reactivation of catalyst

A one-inch internal diameter Hastelloy C reactor
which contained 197 grams of 4 to 8 mesh Guignet's Green
was heated to 500°C. and held at this temperature for about
four hours under a stream of nitrogen. Then, for 98 hours
continuous operation, dichlorodifluoromethane at a rate of
0.184 gram per gram of catalyst per hour was mixed with
anhydrous hydrogen fluoride to provide 4 moles of HF per
mole of CCl_2F_2 and passed through the reactor maintained
at 500°C. The effluent gases from the reactor were scrubbed
with 10% potassium hydroxide solution and dried. At
intervals, samples of the scrubbed and dried product were
collected and analyzed by gas chromatography with the
following results.

Time of sampling, in hours from start	Composition of Product, % by vol.	
	CF_4	$CClF_3$
1.5	78	22
5.	85	15
12.5	88.5	11.5
32	86	14
70	80	20
81	76	24
92	71	29
98	62	38

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The complete replacement of the chlorine by fluorine to form carbon tetrafluoride gradually diminishes, while a partial replacement to form chlorotrifluoromethane continues, and the decreased yield of the tetrafluoromethane is balanced

5   by an increased yield of the trifluoro compound.

The activity of the catalyst, that is diminished by extended use as shown above, may be restored by treatment of the used catalyst with steam. One way in which the catalyst may be reactivated is illustrated by the following

10   procedure. The dichlorodifluoromethane and hydrogen fluoride feeds to the reactor were shut off after the 98 hours' operation indicated above, and the catalyst was allowed to cool to room temperature under a slow stream of nitrogen. The catalyst was then heated to 200°C. to 300°C. and held

15   in this temperature range for eight hours while subjected to the action of a slow stream of nitrogen saturated with water vapor at 75°C. Then the catalyst was heated to 500°C. and held at this temperature for five hours while about 100 g. of water in the form of steam mixed with nitrogen

20   were passed through the reactor tube. Finally, nitrogen alone was passed over the catalyst for three hours. The dichlorodifluoromethane and hydrogen fluoride feeds to the reactor were then resumed at the same rate as before, while the catalyst was held at 500°C. The scrubbed and dried

25   exit gases, after three hours further continuous operation, analyzed 93% carbon tetrafluoride and 7% chlorotrifluoro-methane as compared with 62% CF_4 and 38% $COlF_3$ before reactivating the catalyst.

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Example 9

Fluorination of dichlorodifluoromethane -
Catalyst from precipitated chromium hydroxide

A chromium (III) oxide catalyst was prepared by precipitation of chromium hydroxide from a dilute aqueous
5 solution (0.13 molar) of $CrCl_3 \cdot 6H_2O$ with a slight excess of 0.5 molar ammonium hydroxide. The ammonium hydroxide was added to the stirred solution of chromium chloride hydrate over a period of 5 hours. The precipitate was washed by decantation until it began to peptize, then it
10 was filtered and dried under vacuum, first at 50°C. and finally at 100°C.

This material (70.8 g., about 8 to 20 mesh) was charged to a one-inch Hastelloy C reactor and dehydrated and activated at 400°C. under a slow flow of nitrogen for
15 seven hours. Dichlorodifluoromethane was then fed to the reactor at a rate of 26 g./hr. along with anhydrous hydrogen fluoride at a rate of 17 g./hr. This feed rate is 0.37 g. CCl_2F_2/g. catalyst/hr. with about 4 moles of hydrogen fluoride per mole of CCl_2F_2. The catalyst bed temperature was
20 held at about 400°C. After operating for 1.5 hrs., a sample of the off-gas from the reactor was collected, scrubbed with 10% KOH solution, dried over anhydrous calcium sulfate, and analysed by mass spectrometry. This sample was found to contain 71.0% chlorotrifluoromethane, 28.2% tetrafluoro-
25 methane, and 0.8% dichlorodifluoromethane.

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Example 10

Fluorination of dichlorodifluoromethane - Chrome-Alumina pellets

A one-inch diameter Hastelloy C reactor tube was charged with 221 grams of chrome-alumina catalyst made by
5   The Harshaw Chemical Company in the form of pellets of activated chromium (III) oxide and aluminum oxide. (Cr-0205 T 5/32" Spec. 102 580-218-45). This catalyst analyzed % Al_2O_3 - 78.4, 79.0 and 78.5 and % Cr_2O_3 - 19.6, 19.7, 19.2 and 19.2, and on heating for 2.5 hours at 600°C. lost
10   2.3 and 2.4% weight which apparently was moisture. The catalyst was heated and held at about 540°C. while dichloro-difluoromethane and hydrogen fluoride were fed to the reactor at rates of 0.36 mole/hr. and 0.95 mole/hr., respectively. The effluent gases from the reactor were scrubbed with 10%
15   KOH solution and dried. Samples of the product, taken at intervals, showed the following analyses by mass spectrometry.

Sample No.	1	2
Hrs. "on stream"	2	2-1/3
% $ClCF_3$	76.5	81.8
20 % CF_4	2.1	-
% H_2	14.3	15.2
% CO + N_2	5.7	2.9
% Air	1.3	-

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Example 11

Fluorination of dichlorodifluoromethane - 10' x 2" reactor

A 6.9 lb. quantity of activated chromium (III) oxide catalyst, prepared as described in Example 1 (A), was placed in a 10-foot by 2-inch Inconel reactor and heated to 500°C. Through the reactor, dichlorodifluoromethane was passed at an average rate of 2.95 lb. per hour together with an average input of 1.93 lb. per hour of anhydrous hydrogen fluoride for 80 hours' continuous operation with the temperature held between 500°C. and 550°C. The effluent gases from the reactor were passed through a counter-current water scrubber and through a 15% potassium hydroxide solution, dried over silica gel, and compressed into cylinders. The product, obtained in this way, comprised 99.6% carbon tetrafluoride, 0.2% chlorotrifluoromethane, less than 0.05% dichlorodifluoromethane, and 0.2% air as determined by gas chromatography. With a feed rate of dichlorodifluoromethane of 4.2 lb. per hour and 2.0 lb. per hour of hydrogen fluoride attained at one period of the operation, the scrubbed, dried, and compressed effluent gas still contained more than 99% carbon tetrafluoride.

Example 12

Fluorination of bromotrifluoromethane

An activated chromium (III) oxide catalyst (53 g.), prepared as described in Example 1 (A), was placed in a one-inch diameter Hastelloy C. reactor. The catalyst bed was heated to 500°C. and maintained at about that temperature while a mixture of anhydrous hydrogen fluoride and bromotrifluoromethane in a mole ratio of 4/1 to 5/1 was passed

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through the reactor at a rate of 0.5 g. $BrCF_3$/g. catalyst/hr.
The effluent gases were scrubbed with 10% potassium hydroxide
solution, dried, and analyzed by mass spectrometry. Analysis
indicated that the effluent gas consisted of 95-98% of

5. carbon tetrafluoride.

Example 13

Fluorination of 1,1,2-trichloro-1,2,2-trifluoroethane

An activated chromium (III) oxide catalyst (53 g.),
prepared as described in Example 1 (A), was placed in a one-

10 inch diameter Hastelloy C reactor. The catalyst was held
at 310°C.-320°C. while 20 g./hr. of anhydrous hydrogen
fluoride and 25 g./hr. of 1,1,2-trichloro-1,2,2-trifluoro-
ethane were passed together through the reactor. The
effluent gases from the reactor were scrubbed with 10% KOH

15 solution, dried, and analyzed by mass spectrometry. The
analysis showed a composition of 79.8% dichlorotetrafluoro-
ethane, 17.5% trichlorotrifluoroethane, 0.7% hexafluoroethane
and small quantities of other fluoro compounds.

Example 14

20 ### Fluorination of 1,2-dichlorotetrafluoroethane

Eighty-three grams of an activated chromium (III)
oxide, prepared as described in Example 1 (A) and having a
particle size larger than 80 mesh, was placed in a one-inch
Hastelloy C reactor to form a catalyst bed for the fluori-

25 nation of 1,2-dichlorotetrafluoroethane with anhydrous
hydrogen fluoride. While maintaining the catalyst at fixed
elevated temperatures, a mixture of HF and $CClF_2CClF_2$ in
a mole ratio of 4/1 to 5/1 was passed through the reactor

at the rate of 0.5 g. of $CClF_2CClF_2$/g. catalyst/hr. The effluent gases were scrubbed with 10% potassium hydroxide solution, dried, and analyzed. The results are summarized below.

5	Temp. of catalyst, °C.	Composition of Product, % by vol.	
		CF_3CF_3	$CClF_2CF_3$
	400	13	67
	500	90	6.5
	550	94	4

10 The analyses for the runs at 400°C. and 500°C. were made by gas chromatography and that for the run at 550°C. was made by mass spectroscopy.

Example 15

Fluorination of 1,2-dichlorotetrafluoroethane - 10' x 2" reactor

15   A 10-foot by 2-inch Inconel reactor was charged with 8 lb. of oven-dried chromium (III) oxide gel prepared as described in Example 1 (A). This material was further dehydrated by heating at 500°C. under a slow flow of nitrogen to provide 5.7 lb. of dry activated chromium (III) oxide

20 catalyst. The catalyst was held at a temperature of 400°C. to 425°C. while 1,2-dichlorotetrafluoroethane was fed to the reactor at an average rate of 2.35 lb./hr. together with anhydrous hydrogen fluoride, fed at an average rate of 1.44 lb./hr. The effluent gases from the reactor were passed

25 through a counter-current water scrubber and a 15% KOH solution and dried over silica gel. The dried product was collected by condensation in a steel cylinder cooled by immersion in a bath of solid carbon dioxide-trichloroethylene.

During a period of 57 hours' intermittent operation, 133 lb.

of 1,2-dichlorotetrafluoroethane was fed to the reactor.

The weight of product collected was 109.6 lb. The product,

analyzed by gas chromatography, comprised:

5
          69.8% chloropentafluoroethane
          17.0% hexafluoroethane
          13.2% 1,2-dichlorotetrafluoroethane

This amounts to a 91% yield of fluorinated products which

may readily be separated by distillation.

10
Example 16

Fluorination of 1,2-dichlorotetrafluoroethane -
catalyst as pellets

(A) Pelletized chromium oxide gel catalyst

Chromium (III) oxide, prepared as described in

Example 1 (A) and passed through a 20-mesh screen, was mixed

15 with 2% of its weight of powdered polytetrafluoroethylene

resin and pressed into 3/16" pellets. The pellets were then

placed in a Hastelloy C reaction tube one inch in diameter

and heated slowly to 250°C. under a stream of nitrogen over

a period of four hours. With a continued flow of nitrogen,

20 the temperature was held at 250°C. for two hours and then

raised to 500°C. over a period of seven hours and held at

500°C. for seven hours. The pellets were cooled to room

temperature, removed from the reactor, and sieved to remove

the fine particle dusty material.

25 (B) Fluorination of 1,2-dichlorotetrafluoroethane

Eighty-three grams of the activated chromium (III)

oxide pellets, prepared as described above, were placed as

a catalyst bed in a one-inch diameter Hastelloy C reactor

and heated to 400°C. A mixture of anhydrous hydrogen

fluoride and CClF$_2$CClF$_2$ in a mole ratio of 4/1 to 5/1 was
then passed through the reactor at the rate of about 0.5 g.
of CClF$_2$CClF$_2$/g. catalyst/hr. The effluent gases were
scrubbed with 10% potassium hydroxide solution, dried, and
5 sampled for analysis by mass spectrometry. The procedure
was repeated maintaining the catalyst temperature at 500°C.
The compositions of the product gases were:

Temp. of catalyst °C.	Composition of Product, % by vol.		
	CF$_3$CF$_3$	CClF$_2$CF$_3$	CClF$_2$CClF$_2$
10 400	8.8	51.4	38
500	85.2	10.5	-

The marked effect of raising the temperature from
400°C. to 500°C. on the yield of hexafluoroethane is clearly
shown.

15 ## Example 17

Fluorination of tetrachloroethylene

An activated chromium (III) oxide catalyst (146 g.),
prepared as indicated in Example 1 (A), was placed in a one-
inch Hastelloy C reactor. The catalyst bed was heated and
20 maintained at a temperature of about 400°C. while tetra-
chloroethylene was fed to the reactor at a rate of 33.5 g./hr.
along with anhydrous hydrogen fluoride at a rate of 25 g./hr.
The gaseous effluent from the reactor was scrubbed with 10%
KOH and dried over anhydrous calcium sulfate. Analysis by
25 mass spectrometry showed this material to contain 35.0%
pentafluoroethane, 9.2% 1-chloro-1,2,2,2-tetrafluoroethane,
and 3.5% 1,1-dichloro-2,2,2-trifluoroethane, along with other
materials.

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When the catalyst temperature was held at about 300°C. and feeds to the reactor were maintained as indicated above, the gaseous effluent after rectification was found to contain 38.3% of 1-chloro-1,2,2,2-tetrafluoroethane, 25.4% of pentafluoroethane, 16.0% of 1,1-dichloro-2,2,2-trifluoroethane, and small quantities of other fluorinated products.

Example 18

Fluorination of vinylidene chloride

Activated chromium (III) oxide of greater than 40-mesh in size, prepared as described in Example 1 (A), was charged in an amount of 113 grams into a one-inch Hastelloy C reactor tube and heated to 400°C. A mixture of anhydrous hydrogen fluoride and vinylidene chloride (CH_2=CCl_2) was passed through the reactor at different feed rates. Samples of the exit gases, scrubbed with 10% potassium hydroxide and dried, analysed by mass spectrometry as follows:

Mole ratio of HF/CH_2=CCl_2	Feed rate, g.CH_2=CCl_2/g. catalyst/hr.	Composition of Product, % by vol.			
		CH_3CF_3	CH_2=CF_2	CHCl=CHF	CH_2=CCl_2
2/1	0.5	46.7	3.1	9.2	38.6
4/1	0.25	71.2	1.2	4.5	20.5

A slower feed rate has materially increased the conversion to 1,1,1-trifluoroethane.

Example 19

Fluorination of vinyl chloride

Following the fluorination of 1,2-dichlorotetrafluoroethane in the reactor as described in Example 14, the catalyst was cooled under nitrogen to room temperature.

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Then the catalyst was reheated and while being held at fixed

elevated temperatures a mixture of anhydrous hydrogen fluo-

ride and vinyl chloride in a mole ratio of about 5 to 1 was

passed through the reactor at the rate of 0.16 g. $CH_2=CHCl/g.$

5   catalyst/hr. The effluent gases were scrubbed with 10%

potassium hydroxide solution, dried, and analyzed by mass

spectrometry. The results are summarized below.

Temp. of catalyst, °C.	Composition of Product, % by vol.		
	CH_3CHF_2	$CH_2=CHF$	$CH_2=CHCl$
300-350	32.2	13.7	52.2
400	3.7	30.5	58.6

The product from the reactor at 300°C.-350°C. contained also

a small amount of 1-chloro-1-fluoroethane.

Example 20

Fluorination of chlorotrifluoroethylene

15   A one-inch Hastelloy C reactor was charged with

75 g. of an activated chromium (III) oxide gel catalyst,

prepared as described in Example 1 (A). The catalyst bed

was heated to about 400°C., and chlorotrifluoroethylene was

fed to the reactor at a rate of 25 g./hr. along with anhydrous

20   hydrogen fluoride at a rate of about 25 g./hr. The off-gases

from the reactor were scrubbed with 10% KOH and dried over

anhydrous calcium sulfate. After operating for an hour, a

sample of the off-gas was collected and analyzed by mass

spectrometry. The sample was found to contain 26.8% of

25   pentafluoroethane along with smaller quantities of chloro-

fluoro- and fluoroethanes and ethylenes.

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Example 21

Fluorination of 1,1,1,3-tetrachloro-2,2,3,3-tetrafluoropropane

An activated chromium (III) oxide catalyst (77 g.), prepared as described in Example 1 (A), was placed in a one-
5. inch diameter Hastelloy C reactor. The reactor was connected at its bottom end to a 500 ml. copper pot which was immersed in an ice bath. The catalyst bed was maintained at a temperature of 200°C. while 25 g./hr. of anhydrous hydrogen fluoride together with 28 g./hr. of 1,1,1,3-tetrachloro-
10 2,2,3,3-tetrafluoropropane were fed to the reactor. A total of 47 g. of the tetrachlorotetrafluoropropane was fed to the reactor over a period of 100 minutes. The feeds were then shut off, the reactor was purged with nitrogen and the liquid products, which had collected in the copper pot, were poured
15 onto 200 g. of ice. The mixture was stirred and neutralized with potassium hydroxide. The water-insoluble organic phase (30.1 g.) was drawn off and distilled through a small spinning band distillation column. It boiled at 72°C.-73°C. The product so collected was identified as 1,1,3-trichloro-
20 1,2,2,3,3-pentafluoropropane by the following analyses:

	Product (Found)	$Cl_2CFCF_2CF_2Cl$
Refractive Index	$1.3513^{20°}$	$1.3578^{25°}$
Density	$1.6445 \frac{20}{20}$	$1.6429^{25°}$
Molecular Weight	233, 237	237.35
25 % Chlorine	44.3, 44.5	44.8 (ca.)
% Fluorine	40.0, 40.1	40.0 (ca.)
% Carbon	15.1, 15.3	15.16 (ca.)

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When the catalyst temperature was held at 400°C.
and 25 g. to 35 g./hr, of anhydrous hydrogen fluoride
together with 24 g./hr. of the tetrachlorotetrafluoropropane
were fed, no liquid organic product was collected. The
5   gaseous effluent from the reactor was scrubbed with 10% KOH,
dried, and analyzed by gas chromatography. It was found to
consist of about 20% perfluoropropane, about 80% 1-chloro-
heptafluoropropane and small quantities of other unidentified
materials.

10   When the catalyst temperature was held at 500°C.,
and feeds to the reactor were maintained as given immediately
above, the gaseous effluent from the reactor was found by
gas chromatography to contain about 40% of perfluoropropane
along with some 1-chloroheptafluoropropane and other
15   unidentified materials.

Example 22

Fluorination of 1,2-dichlorohexafluoropropane

Chromium oxide gel (10 lb.), prepared with oven
drying as described in Example 1 (A), was further dehydrated
20   at 500°C. in a 10-foot x 2-inch Inconel reactor under a slow
stream of nitrogen to yield 6.9 lb. of activated catalyst.
The catalyst bed temperature was adjusted to about 425°C.
before 1,2-dichlorohexafluoropropane was metered to the
reactor at 0.44 lb./lb. catalyst/hr. together with sufficient
25   anhydrous hydrogen fluoride to maintain a $HF/CF_3CHClCF_2Cl$
molar ratio of 5/1 in the feed stream. The gaseous effluent
from the reactor was scrubbed first with water and then
with 10% potassium hydroxide solution, dried over silica gel,
and condensed in a cold receiver. The water and potassium

hydroxide scrubbers and the drying tube were maintained at 45°C. The yield, based on recovered organic products, was 96.7%. The composition of the product, determined by gas chromatography was:

5
2-chloroheptafluoropropane	78%
octafluoropropane	1%
1,2-dichlorohexafluoropropane	21%

An organic feed, consisting of 80% by volume of 2-chloroheptafluoropropane and 20% by volume of 1,2-dichloro-
10 hexafluoropropane, was then metered to the reactor at 0.22 lb./lb. catalyst/hr. along with sufficient hydrogen fluoride to maintain a hydrogen fluoride/organic composition molar ratio of 4/1 and the temperature of the catalyst bed was increased slowly from 450°C. to 625°C. The conversion to
15 octafluoropropane, determined by gas chromatography analysis of the scrubbed and dried reactor effluent, was:

Reactor Temperature °C.	Vol. % $CF_3CF_2CF_3$ in effluent gas
490-520	17
520-535	28
535-575	50
575-610	70
610-625	80

Example 23

Fluorination of 2,3-dichlorooctafluorobutane

25   Into a 3/4" Hastelloy C reactor tube was charged 186 g. of chromium oxide gel catalyst, prepared with oven drying as described in Example 1 (A), and dehydrated in the reactor at 500°C. under a slow stream of nitrogen. The temperature of the catalyst was then adjusted to 450°C.,
30 and 2,3-dichlorooctafluorobutane was metered to the reactor at 0.30 g./g. catalyst/hr. along with sufficient anhydrous

hydrogen fluoride to maintain an $HF/C_4F_8Cl_2$ mole ratio of
4.5/1 in the feed stream. The reactor effluent was scrubbed
with 15% KOH, dried over silica gel and condensed in a cold
trap. The scrubber and drying tube were maintained at 65°C.
5   About 95 g. of $C_4F_8Cl_2$ was fed to the reactor before the
experiment was terminated. The cold trap contained 68 g.
of product which was shown by gas chromatography to have
the following composition.

C_4F_{10}	10%
10	C_4F_9Cl	38%
$C_4F_8Cl_2$	37%
unidentified	15%

Example 24

Fluorination of 1,4-dibromooctafluorobutane

15   In a Hastelloy C reactor, 126.5 g. of chromium
oxide, prepared with oven drying as described in Example
1 (A), was further dehydrated under a slow stream of nitrogen
at 500°C. to provide 88 g. of anhydrous activated catalyst.
The catalyst temperature was adjusted to 350°C., and 1,4-
20   dibromooctafluorobutane was metered at 0.57 g./g. catalyst/
hr. along with sufficient hydrogen fluoride to maintain an
$HF/C_4F_8Br_2$ mole ratio of 4/1. The reactor effluent was
scrubbed in 15% KOH, dried over silica gel and condensed in
a cold trap. The scrubber and drying tube were maintained
25   at 50°C. Unconverted starting material, collected in a
trap maintained at 50°C. and connected to the bottom of the
reactor, was combined with the condensed products from the
drier for analysis. Analysis by gas chromatography indicated
that the product had the following composition.

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$$C_4F_{10} \qquad 5\%$$
$$C_4F_9Br \qquad 60\%$$
$$C_4F_8Br_2 \qquad 30\%$$
$$\text{unidentified} \quad 5\%$$

The catalyst temperature was then increased to
500°C, with the same feed conditions. Gas chromatography
analysis of the scrubbed reactor effluent indicated that
decafluorobutane was now formed in an amount of about 50%
of the product.

Example 25

Fluorination of 1,1,1,7-tetrachlorododecafluoroheptane

An activated chromium (III) oxide gel catalyst
(100 g.), prepared as described in Example 1 (A), was placed
in a one-inch diameter Hastelloy C reactor. The reactor
was connected at its bottom end to a 500 ml. copper pot
which was immersed in an ice bath. The catalyst bed was
maintained at a temperature of about 400°C. while 25 g./hr.
of anhydrous hydrogen fluoride together with about 12 g./hr.
of 1,1,1,7-tetrachlorododecafluoroheptane was fed to the
reactor. A total of 49 g. of the tetrachlorododecafluoro-
heptane was fed to the reactor over a period of about four
hours. The feeds were then shut off, the reactor was purged
with nitrogen and the liquid products which had collected
in the copper pot were poured onto 200 g. of ice. The water
insoluble organic phase was drawn off, washed with 5% sodium
bicarbonate solution and dried over anhydrous calcium sulfate.
The dried material was filtered to remove the drying agent,
and distilled through a small spinning band distillation
column. There was obtained a 51% yield of perfluoroheptane

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containing a small amount of a lesser fluorinated derivative and identified by the following analysis.

Calculated for C_7F_{16}: C - 21.6%, F - 78.4%

Found: C - 20.6%, F - 77.5%

5   Boiling point: Lovelace et al.[*]: 82°C.
                                Observed: 82°C.

[*]Aliphatic Fluorine Compounds, Reinhold Pub. Co. 1958, p. 75.

In addition, there was obtained a 36% yield of chloropentadecafluoroheptane identified by the following analysis.

10   Calculated for $C_7F_{15}Cl$: C - 20.8%, Cl - 8.8%, F - 70.5%

Found: C - 20.9%, Cl - 8.5%, F - 70.7%

Boiling point: 109°C.

Example 26

Fluorination of 1,6-dibromododecafluorohexane

15   An activated chromium (III) oxide gel catalyst (89 g.), prepared as described in Example 1 (A), was placed in a 3/4" diameter Hastelloy C reactor. To the bottom of the reactor was connected a 500 ml. copper receiver immersed in an ice bath. While maintaining the catalyst temperature

20   at 350°C., 1,6-dibromododecafluorohexane was passed through the reactor at a rate of 100 g./hr. together with anhydrous hydrogen fluoride to give an $HF/C_6F_{12}Br_2$ mole ratio of 2/1. The product that collected in the copper receiver was poured into ice water. The separated organic layer was withdrawn,

25   washed with dilute sodium bicarbonate solution, and dried. Gas chromatography analysis of the product revealed the following composition.

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$$C_6F_{14} \qquad 19.4\%$$
$$C_6F_{13}Br \qquad 7.6\%$$
$$C_6F_{12}Br_2 \qquad 69.6\%$$
$$\text{unidentified} \qquad 3.4\%$$

Example 27

Fluorination of 1,2,4-trichloropentafluorocyclopentene

An activated chromium (III) oxide gel catalyst
(100 g.), prepared as described in Example 1 (A), was placed
in a one-inch diameter Hastelloy C reactor. The reactor was
connected at its bottom end to a 500 ml. copper pot which
was immersed in an ice bath. The catalyst bed was heated
and maintained at a temperature of about 400°C. while an-
hydrous hydrogen fluoride at about 25 g./hr. and 1,2,4-
trichloropentafluorocyclopentene at about 26 g./hr. were
fed to the reactor. The reaction was continued in this way
for a period of 2.5 hours. The feeds were then turned off,
the reactor was purged with nitrogen, and the liquid
products which had collected in the copper pot were poured
onto 200 g. of ice. The water insoluble organic phase was
drawn off, washed with 5% sodium bicarbonate solution, and
dried over anhydrous calcium sulfate. The dried product
was filtered and distilled through a small spinning band
column. Three main distillation cuts were obtained.

Cut #1	Boiling range	45°C.-88°C.	3.9 g.
Cut #2		88°C.-89°C.	27.0 g.
Cut #3		89°C.-116°C.	3.5 g.

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Cut #2 is 1,2-dichlorohexafluorocyclopentene as identified by nuclear magnetic resonance and chemical analysis.

Calculated for $C_5F_6Cl_2$: C - 24.5%, F - 46.5%, Cl - 24.5%
5   M.W. - 245.

Found: C - 24.2%, F - 46.3%, Cl - 24.2%, M.W. - 250.

Example 28

Fluorination of α,α,α-trichlorotoluene

A one-inch Hastelloy C reactor was charged with
10 94 g. of chromium oxide gel catalyst prepared as described in Example 1 (A). The reactor was connected at its bottom end to a 500 ml. copper receiver immersed in an ice bath. The catalyst was heated to 400°C., and a mixture of anhydrous hydrogen fluoride and dry nitrogen was passed through the
15 reactor for 30 minutes. Then 62.5 g. of α,α,α-trichloro- toluene was fed to the reactor over a period of 1.5 hrs. together with anhydrous hydrogen fluoride at an average rate of 20 to 25 g. per hr. while maintaining the tempera- ture of the catalyst at 400°C. The product of the reaction
20 and excess hydrogen fluoride which collected in the copper receiver were poured onto about 200 g. of ice and stirred briefly. On standing, a water-insoluble lower layer separated. This layer was drawn off, washed with a 5% solution of sodium acid carbonate, dried over anhydrous
25 calcium sulfate, and distilled. A product having a boiling point of 100°C., and amounting to 15.3 g. was identified by molecular weight determination and chemical analysis as α,α,α-trifluorotoluene.

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Calculated for $C_7H_5F_3$: M.W. - 146, F - 39.0%, Cl - 0.0%

Found: M.W. - 146, 149, F - 39.0%, 39.3%, Cl - 0.2%

The data of the Examples are summarized below
in tabular form for the purpose of providing a convenient
5 reference thereto. In that Summary, Gel designates the
catalyst obtained from the chromium oxide gel resulting
from the reduction of CrO_3 with ethanol; GG designates the
catalyst prepared from Guignet's Green; -OH ppt designates
the catalyst prepared from chromium hydroxide precipitated
10 from $CrCl_3$ with ammonia. Also, the volume % of particular
products in the gaseous products are indicated in
parentheses ( ).

SUMMARY OF EXAMPLES

Ex.	Reactant with HF	Form of Cr₂O₃ Catalyst	Temp. of Catalyst °C.	Main Products
1	CCl₄	Gel	150	CCl₂F₂(97)
2	CCl₄	Gel	400	CF₄(94)
3	CCl₄	GG	200	CCl₂F₂(84), CCl₃F(15)
4	CHCl₃	Gel	400	CHF₃(96)
5	CH₃Cl	Gel	250	CH₃F(6.5)
6	CCl₂F₂	Gel	200	CClF₃(ca. 70)
	"	"	300	CF₄(67), CClF₃(33)
	"	"	400	CF₄(97)
	"	"	500	CF₄(>98)
	"	No catalyst	550	CClF₃(10)
	"	"	600	CClF₃(35)
7	CCl₂F₂	GG	200	CClF₃(Trace)
	"	"	300	CClF₃(99)
	"	"	400	CClF₃(52), CF₄(48)
	"	"	500	CF₄(92), CClF₃(8)

SUMMARY OF EXAMPLES (Cont'd)

Ex.	Reactant with HF	Form of Cr_2O_3 Catalyst	Temp. of Catalyst, °C.	Main Products
8	CCl_2F_2	GG	500	CF_4(62 to 89), $CClF_3$(38 to 11)
"	"	GG, reactivated	500	CF_4(93-43), $CClF_3$(7-57)
9	CCl_2F_2	-OH ppt.	400	$CClF_3$(71), CF_4(28)
10	CCl_2F_2	Chrome-Alumina pellets	540	$CClF_3$(79)
11	CCl_2F_2	Gel in 10' x 2" reactor	500-550	CF_4(99)
12	$CBrF_3$	Gel	500	CF_4(98)
13	CCl_2FCClF_2	Gel	315	$C_2Cl_2F_4$(80), CF_3CF_3(0.7)
14	$CClF_2CClF_2$	Gel	400	$CClF_2CF_3$(67), CF_3CF_3(13)
"	"	"	500	CF_3CF_3(90), $CClF_2CF_3$(6.5)
"	"	"	550	CF_3CF_3(92), $CClF_2CF_3$(4)
15	$CClF_2CClF_2$	Gel in 10' x 2" reactor	400-425	$CClF_2CF_3$(70), CF_3CF_3(17)
16	$CClF_2CClF_2$	Gel, pellets	400	$CClF_2CF_3$(51), CF_3CF_3(9)
"	"	"	500	CF_3CF_3(85), $CClF_2CF_3$(11)
17	$CCl_2=CCl_2$	Gel	400	CHF_2-CF_3(35), $CHClFCF_3$(9)
18	$CH_2=CCl_2$	Gel	400	CH_3CF_3(47,71)

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SUMMARY OF EXAMPLES (Cont'd)

Ex.	Reactant with HF	Form of Cr_2O_3 Catalyst	Temp. of Catalyst, °C.	Main Products
19	$CH_2=CHCl$	Gel	300-350	$CH_3CHF_2(32)$, $CH_2=CHF(14)$
	"	"	400	$CH_2=CHF(31)$, $CH_3CHF_2(4)$
20	$CClF=CF_2$	Gel	400	$CHF_2CF_3(27)$
21	$CCl_3CF_2CF_2Cl$	Gel	200	$CCl_2FCF_2CF_2Cl$
22	$CF_3CClFCClF_2$	Gel	425	$CF_3CClFCF_3(78)$, $C_3F_8(1)$
	$CF_3CClFCF_3(80)$ / $CF_3CClFCClF_2(20)$	"	490-625	$C_3F_8(17$ to $>80)$
23	$CF_3CClFCClFCF_3$	Gel	450	$C_4F_9Cl(38)$, $C_4F_{10}(10)$
24	$BrCF_2CF_2CF_2CF_2Br$	Gel	350	$C_4F_9Br(60)$, $C_4F_{10}(5)$
	"	"	500	$C_4F_{10}(50)$
25	$Cl_3C(CF_2)_5CF_2Cl$	Gel	400	$C_7F_{16}(50)$, $C_7F_{15}Cl(36)$
26	$BrCF_2(CF_2)_4CF_2Br$	Gel	350	$C_6F_{14}(19)$, $C_6F_{13}Br(8)$
27	$CF_2CClFCF_2CCl=CCl$	Gel	400	Cyclic $C_5F_6Cl_2$
28	⬡–CCl_3	Gel	400	⬡–CF_3

It will be understood that the preceding Examples are given for illustrative purposes solely and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be readily apparent to those skilled in the art that, subject to the limitations set forth in the general description, many variations can be made in the materials, the proportions, the conditions, and the techniques employed, without departing from the spirit or scope of this invention.

From the preceding description, it will be apparent that this invention provides a new and improved process for preparing a wide variety of valuable products, particularly many compounds which heretofore were difficult and expensive to produce. The process is simple, economical, and easy to operate and control so as to produce selected products as desired. Particularly, it produces exceptionally high yields of the desired products, especially of compounds which could not heretofore be produced except with difficulty and at high cost. Accordingly, it will be apparent that this invention constitutes a valuable contribution to and advance in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for fluorinating halohydrocarbons which comprises contacting a vapor mixture of

(a) a halogenated unsaturated aliphatic hydrocarbon of 2 to 6 carbon atoms in which at least one of the adjacent carbon links is a 2 valence bond and in which the halogen atoms have an atomic weight of less than 80 and include at least one halogen atom having an atomic weight between 35 and 80, said hydrocarbon being selected from the group consisting of

$CF_2=CFBr$	$CF_2=CFCF_2Cl$
$BrCF=CFBr$	$CF_2=CClCF_3$
$CF_2=CBr_2$	$CCl_2=CFCF_3$
$CFBr=CBr_2$	$CF_2=CFCCl_3$
$CFBr=CHF$	$CF_2=CFCFCl_2$
$CF_2=CHBr$	$CCl_2=CClCF_3$
$CFBr=CHBr$	$CF_2=CHCF_2Br$
$Cl_2C=CCl_2$	$CHCl=CFCF_2Cl$
$ClCH=CCl_2$	$CCl_2=CHCF_2Cl$
$ClCH=CHCl$	$CH_2=CBrCF_3$
$CH_2=CCl_2$	$CF_3CF_2CClFCF=CClF$
$CF_2=CFCl$	$CF_2ClCF=CFCF_2Cl$
$ClCF=CFCl$	$CF_2=CFCFClCF_2Cl$
$CF_2=CCl_2$	$CF_2ClCH_2CH=CH_2$
$CFCl=CCl_2$	$CFCl=CHCH_2CH_3$
$CHCl=CBr_2$	$CF_2CFBrCFBrCF_2CF=CF$
$CHCl=CF_2$	$CF_2CCl_2CCl_2CCl=CCl$
$CHF=CHCl$	$CF_2CCl_2CFClCCl=CCl$
$CH_2=CBr_2$	$CF_2CFClCF_2CCl=CCl$

and,

(b) at least a stoichiometric proportion of anhydrous hydrogen fluoride,

48
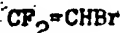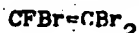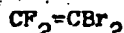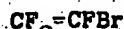
with a catalyst which consists essentially of an activated
anhydrous chromium (III) oxide at a temperature in the range
of from about 150°C. to about 700°C. such that the principal
reaction is the substitution of fluorine for other halogen of
the halogenated hydrocarbon, and separating the fluorinated
compound from the reaction mixture.

2. The process for fluorinating halohydrocarbons
which comprises contacting a vapor mixture of

(a) a halogenated unsaturated acyclic hydrocarbon of
2 to 6 carbon atoms in which at least one of the
adjacent carbon links is a 2 valence bond and in
which the halogen atoms have an atomic weight of
less than 80 and include at least one halogen atom
having an atomic weight between 35 and 80, said
hydrocarbon being selected from the group consisting
of

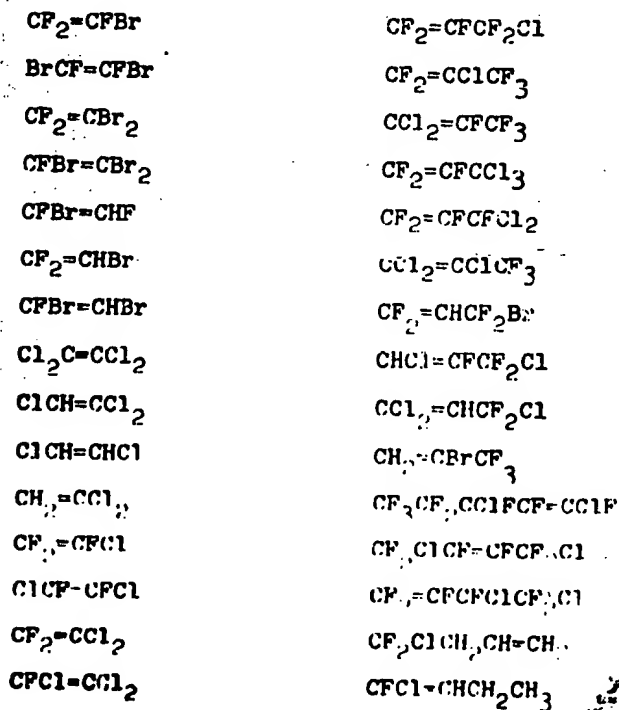|	
$CF_2=CFBr$	$CHF=CHCl$
$BrCF=CFBr$	$CH_2=CBr_2$
$CF_2=CBr_2$	$CF_2=CFCF_2Cl$
$CFBr=CBr_2$	$CF_2=CClCF_3$
$CFBr=CHF$	$CCl_2=CFCF_3$
$CF_2=CHBr$	$CF_2=CFCCl_3$
$CFBr=CHBr$	$CF_2=CFCFCl_2$
$Cl_2C=CCl_2$	$CCl_2=CClCF_3$
$ClCH=CCl_2$	$CF_2=CHCF_2Br$
$ClCH=CHCl$	$CHCl=CFCF_2Cl$
$CH_2=CCl_2$	$CCl_2=CHCF_2Cl$
$CF_2=CFCl$	$CH_2=CBrCF_3$
$ClCF=CFCl$	$CF_3CF_2CClFCF=CClF$
$CF_2=CCl_2$	$CF_2ClCF=CFCF_2Cl$
$CFCl=CCl_2$	$CF_2=CFCFClCF_2Cl$
$CHCl=CBr_2$	$CF_2ClCH_2CH=CH_2$
$CHCl=CF_2$	$CFCl=CHCH_2CH_3$
and,	

(b) at least a stoichiometric proportion of anhydrous

hydrogen fluoride,

with a catalyst which consists essentially of an activated an-
hydrous chromium (III) oxide at a temperature in the range of
from about $150^\circ C.$ to about $700^\circ C.$ such that the principal
reaction is the substitution of fluorine for other halogen of
the halogenated hydrocarbon, and separating the fluorinated
compound from the reaction mixture.

3.   The process for fluorinating halohydrocarbons
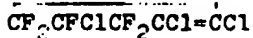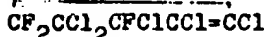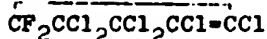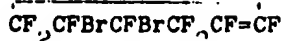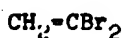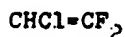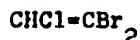which comprises contacting a vapor mixture of

(a) a halogenated unsaturated aliphatic hydrocarbon of
2 to 6 carbon atoms in which at least one of the
adjacent carbon links is a 2 valence bond and in
which the halogen atoms have an atomic weight of
less than 80 and include at least one halogen atom
having an atomic weight between 35 and 80, said
hydrocarbon being selected from the group consisting
of

$CF_2=CFBr$	$CF_2=CFCF_2Cl$
$BrCF=CFBr$	$CF_2=CClCF_3$
$CF_2=CBr_2$	$CCl_2=CFCF_3$
$CFBr=CBr_2$	$CF_2=CFCCl_3$
$CFBr=CHF$	$CF_2=CFCFCl_2$
$CF_2=CHBr$	$CCl_2=CClCF_3$
$CFBr=CHBr$	$CF_2=CHCF_2Br$
$Cl_2C=CCl_2$	$CHCl=CFCF_2Cl$
$ClCH=CCl_2$	$CCl_2=CHCF_2Cl$
$ClCH=CHCl$	$CH_2=CBrCF_3$
$CH_2=CCl_2$	$CF_3CF_2CClFCF=CClF$
$CF_2=CFCl$	$CF_2ClCF=CFCF_2Cl$
$ClCF=CFCl$	$CF_2=CFCFClCF_2Cl$
$CF_2=CCl_2$	$CF_2ClCH_2CH=CH_2$
$CFCl=CCl_2$	$CFCl=CHCH_2CH_3$

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CHCl=CBr$_2$	CF$_2$CFBrCFBrCF$_2$CF=CF$_2$
CHCl=CF$_2$	CF$_2$CCl$_2$CCl$_2$CCl=CCl
CHF=CHCl	CF$_2$CCl$_2$CFClCCl=CCl
CH$_2$=CBr$_2$	CF$_2$CFClCF$_2$CCl=CCl

and,

(b) at least a stoichiometric proportion of anhydrous
    hydrogen fluoride,

with a catalyst at a temperature in the range of from about 150°C.
to about 700°C. such that the principal reaction is the substi-
tution of fluorine for other halogen of the halogenated hydrocar-
bon, said catalyst consisting essentially of an activated
anhydrous chromium (III) oxide gel, made by reducing chromium
trioxide with ethanol and then dehydrating the reduced product
at a temperature of from about 400°C. to about 600°C. in an
inert atmosphere, and separating the fluorinated compound from
the reaction mixture.

4. A process which comprises contacting, in the
vapor phase, hydrogen fluoride with a compound selected from
the group consisting of perchlorofluoroethylene and tetrachloro-
ethylene with an activated anhydrous chromium (III) oxide
catalyst at a temperature between 200°C. and 550°C. and recovering
pentafluoroethane as product.

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